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## Phase Relationships of Polyioncomplex Composed of Sodium-Polystyrene Sulfonate and Polyvinyl Pyridinium Bromide in Three-Component Solvent Systems

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Phase equilibria of sodium-polystyrene sulfonate (polyanion), polyvinyl pyridinium bromide (polycation), and polyioncomplex composed of these two polyelectrolytes were investigated in three-component solvent systems: acetone-water-NaBr, and acetone-water-CaCl<sub>2</sub>. It was found that an equivalent mixture of polyanion and polycation formed polyioncomplex and thus obtained complex was soluble in a limited composition range of the solvent systems used. In this range of aqueous solvent systems, such salt as NaBr or CaCl<sub>2</sub> may act to loosen the ionic interactions between the polyanion and polycation, while acetone may act on and stabilize the hydrophobic chain portions of these two polymers.

### I. INTRODUCTION

Since the coacervation phenomena in aqueous systems of polycation and polyanion were first investigated by Bungenberg de Jong,<sup>1)</sup> interaction between polyelectrolytes with opposite signs has been discussed as functions of temperature, *pH*, solvent composition and ionic strength. Coacervation concerns with interaction *i.e.*, partial miscibility in a rather physico-chemical sense, between weakly charged polyelectrolytes, especially in concentrated solution range. Coacervation may disappear by dilution. Neutral salts may act not to disturb but rather accelerate the coacervation phenomena.

On the other hand, if electrostatic attraction between polyelectrolytes with opposite signs is so strong as to form a perfect precipitate, then so-called complexcoacervation<sup>1)</sup> is realized in aqueous media. The complexcoacervation is observed only in dilute solution, and is disturbed by neutral salt when the ionic strength is remarkably high.

Theoretical treatment on complexcoacervation, however, is not sufficient except some schematic calculations on the effect of 1-1 electrolyte. Michaeli and others<sup>2)</sup> presented a phase diagram for complexcoacervation in a system containing equivalent amounts of polycation P<sup>+</sup> and polyanion Q<sup>-</sup>, microions K<sup>+</sup> and A<sup>-</sup>, and water, assuming that the macroions are identical except for the sign of their charge, and the same is for the microions. Such system was treated as a three-component system, the components being H<sub>2</sub>O, K<sup>+</sup>A<sup>-</sup>, and the polymer P<sup>+</sup>Q<sup>-</sup>.

With regard to the interaction between strong polycations and polyanions, Fuoss and Saddek<sup>3)</sup> first pointed out that, the interaction between these two polyelectrolytes

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resulted in a stoichiometric compound composed of both components. Further researches have been carried out by Michaels and Miekka,<sup>49</sup> and Michaels,<sup>50</sup> on such polyelectrolyte complex as prepared from sodium-polystyrene sulfonate and polyvinyl-benzyl-trimethyl-ammonium chloride.

In this study, phase equilibria of a polyioncomplex (PC) composed of sodium-polystyrene sulfonate (PSS-Na) and poly-2-vinyl pyridinium bromide (PVP-Br), *i.e.*,



in three-component solvent systems will be discussed. The solvent systems used are acetone-water-NaBr, and acetone-water-CaCl<sub>2</sub>. Such solvent systems were used by the reason that the presence of NaBr or CaCl<sub>2</sub> only in water was not sufficient but also the addition of acetone was necessary to dissolve the polyioncomplex. In this work, the polyioncomplex containing equivalent amount of polycation and polyanion was examined exclusively.

## II. EXPERIMENTAL

### 1. Synthesis of Polycation

Purified 2-vinyl pyridine was dissolved in petroleum ether and polymerized in the presence of benzoyl peroxide as initiator under nitrogen atmosphere at 45-50°C for 5 days, according to the method proposed by Strauss.<sup>61</sup> Poly-2-vinyl pyridine thus obtained was washed with petroleum ether, then dissolved in toluene-pyridine mixture and again precipitated and washed in petroleum ether. The molecular weight of the purified poly-2-vinyl pyridine was estimated from intrinsic viscosity  $[\eta]$  (dl/g) measured in methanol at 25°C, applying the relation proposed for poly-4-vinyl pyridine<sup>79</sup>:  $[\eta] = 2.5 \times 10^{-4} M^{0.68}$ . From measured value of  $[\eta] = 0.566$ , the molecular weight  $M$  was estimated as  $M = 8.6 \times 10^4$  (degree of polymerization = 820).

The polymer then quarternized with equivalent amount of hydrobromic acid in aqueous system to yield poly-2-vinyl pyridinium bromide (PVP-Br), which behaves as polycation in water.

### 2. Synthesis of Polyanion

Sodium styrene sulfonate was polymerized in a 25% monomer-75% water mixture by the use of potassium persulfate and sodium bisulfite as initiators under nitrogen atmosphere and agitation at 45 - 50°C, according to the method of R.H.Wiley.<sup>81</sup> The polymerized product was dialyzed for 3 days, then dried in a rotary evaporator and further dried in vacuo.

Relation between the molecular weight and intrinsic viscosity is not known for this polymer. However, with the aid of samples of known molecular weight, the molecular weight of the sample prepared was estimated by interpolation from the intrinsic

viscosity values measured in 0.1N-NaBr aqueous solutions at 25°C. From measured value of  $[\eta] = 3.225$ , it was estimated that  $M = 3.6 \times 10^5$  (degree of polymerization = 1740).

The equivalent amount of NaOH was added to the polymer prepared by dialysis to yield sodium-polystyrene sulfonate (PSS-Na), which acts as polyanion in water.

### 3. Preparation of Polyioncomplex

A 0.2 g/dl aqueous solution of sodium-polystyrene sulfonate (PSS-Na) was added dropwise under agitation to a 0.2 g/dl of aqueous solution of poly-2-vinyl pyridinium bromide (PVP-Br), resulting in the formation of white precipitate. Agitation was continued for 30 min, still after the end of reaction. White featherlike precipitates were gathered by decantation, then washed with water-acetone (4 : 6 by volume) mixture to remove excess  $\text{Na}^+$  and  $\text{Br}^-$  ions together with unreacted poly-electrolyte molecules. By drying the precipitates, white power-like polyioncomplex (PC) was obtained, the yield of which was about 75% by weight. The results on elemental analysis, S: 9.05 and N: 4.84, may be compared with theoretical values of S: 11.12 and N: 4.86, calculated by assuming an equivalent reaction product. The reason for lower observed value of S is not definite but one supposed reason may be that some sulfonyl residues are lost during polymerization process.

### 4. Experiments of Phase Relationships

In the first place, mutual miscibility of the components in the solvent systems, *i.e.*, acetone-water-NaBr, and acetone-water- $\text{CaCl}_2$ , was examined. When NaBr (or  $\text{CaCl}_2$ ) is added to acetone-water mixture, first liquid-liquid separation takes place and further addition of the salt results in liquid-liquid-solid separation. In this experiment, phase diagrams were obtained by determining the compositions at boundary for liquid-liquid phase separation.

In the next place, the miscibility of polycation, polyanion, or polyioncomplex in the three-component solvent systems mentioned above was examined. The concentrations of polymer in solvent mixtures used here was in a range of 0.2 - 0.5 weight-%. The phase diagrams were obtained by determining the composition at which the solution just began to become turbid. Within the range of polymer concentration used, the difference in polymer concentration was found not to influence on the composition of boundary point.

## III. RESULTS AND DISCUSSION

Results in the systems acetone-water-NaBr and acetone-water- $\text{CaCl}_2$  were shown in Figs.1 and 2, respectively, in which the composition was given in weight-% of the components. The mutual miscibility of the components in these three-component solvent mixtures, in the absence of polymer component, was given by the broken curve in each figure. The left side of this curve is the region in which the components are mutually miscible perfectly. So the experiments on systems including polymers were, as a matter of course, carried out in such solvent composition range.

The phase diagrams for PSS-Na and PVP-Br in acetone-water-NaBr system were seen in Fig.1. Also in these cases, the left side of the curves denotes the region in which

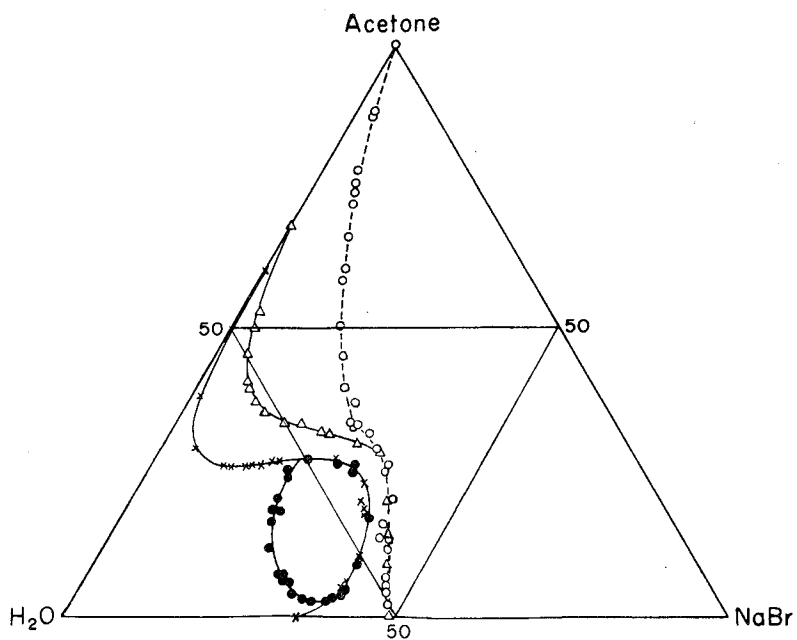


Fig. 1. Phase diagrams of polyioncomplex (●), sodiumpolystyrene sulfonate (×), and polyvinyl pyridinium bromide (△) in acetone-water-NaBr system at 30°C. Broken line (○) denotes the boundary for miscibility among solvent components, in the absence of polymer.

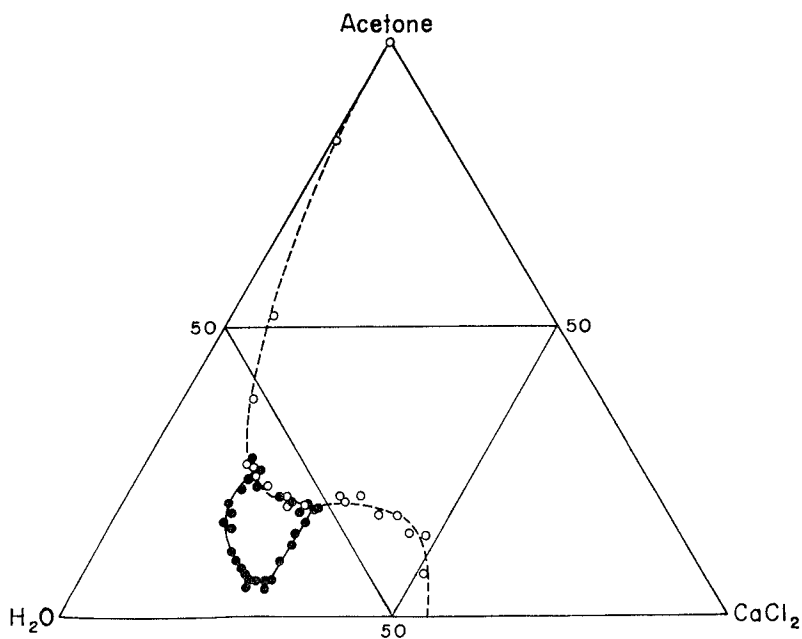


Fig. 2. Phase diagram of polyioncomplex (●) in acetone-water- $\text{CaCl}_2$  system at 30°C. Broken line (○) denotes the boundary for miscibility among solvent components, in the absence of polymer.

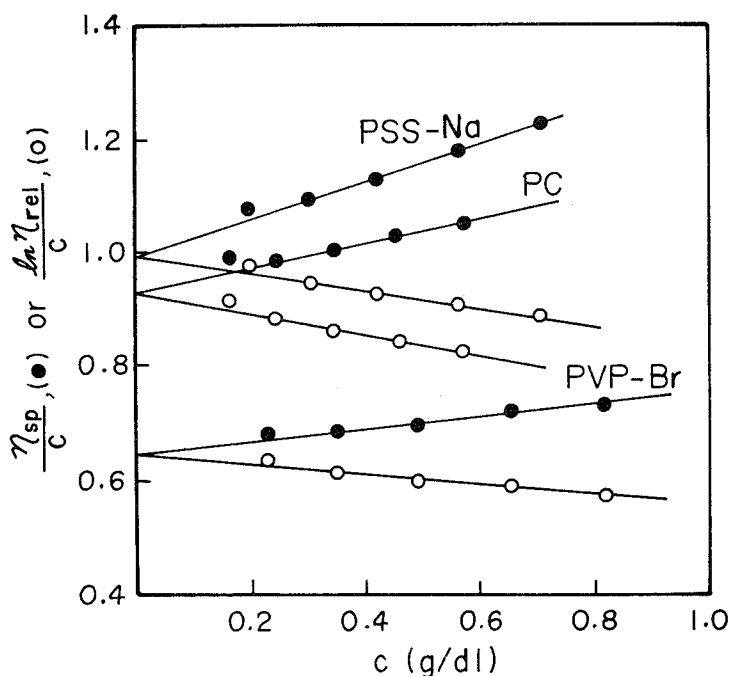


Fig. 3. Viscosities of PSS-Na, PVP-Br, and PC in acetone-water-NaBr (18 : 51 : 31 weight-%) mixture, at 30°C.

the polymer component is soluble. The curve for PSS-Na locates more left side than that for PVP-Br. This means that PVP-Br requires more NaBr and acetone to separate into phases. In other words, PVP-Br is less hydrophobic than PSS-Na, and escaping ability of the  $\text{Br}^-$  ions from the polycation  $\text{P}^+$  is less than that of  $\text{Na}^+$  ions from the polyanion  $\text{Q}^-$ . In this sense, the present system including PSS-Na and PVP-Br is not symmetrical with regard to neither polycation and polyanion, nor micro cation and micro anion. But unsymmetry of the ionic character is said not to be remarkable.

The phase diagram of PC is circular in form. This curve partly coincides with the curve for PSS-Na. Within the circular curve, components were perfectly miscible and thus formed transparent solution. In this case, polyanion and polycation may locate separately, being hydrated, and gegen ions  $\text{Na}^+$  and  $\text{Br}^-$  may be restricted to occupy small volume near the polyanion and polycation. But outside of this circle, polyanion and polycation forms polyioncomplex, thus separation into phases does occur.

Figure 2 shows the effect of bi-valent cation  $\text{Ca}^{++}$ . In this case, the boundary curve for solvent mixture without containing polymer component shifts to the left compared with that shown in Fig.1. The boundary curve for PC in this solvent mixture also shifts to the left in comparison with that for system including NaBr. Such result is to be attributable to that the charge density of  $\text{Ca}^{++}$  is larger than that of  $\text{Na}^+$ , so smaller amount of  $\text{Ca}^{++}$  can dissolve the PC and at the same time salting-out effect of  $\text{Ca}^{++}$  on PSS-Na is larger than that of  $\text{Na}^+$ .

Michaels and Miekka<sup>49</sup> have pointed out that the polyioncomplex produced from a 1:1 mole polyvinyl-benzyl-trimethyl-ammonium chloride and sodium-polystyrene sulfonate mixture does not contain micro ion at all. The same seems also true for the

Table 1. Intrinsic Viscosities of PC, PSS-Na, and PVP-Br in Acetone-Water-NaBr (18 : 51 : 31 Weight-%) Mixture at 30°C, Compared with that Calculated for 1 : 1 Mole Mixture of Polycation and Polyanion Assuming additivity of  $[\eta]$  with Weight Fraction.

Polymer	$[\eta]$ (dl/g)
PC	0.923
PSS-Na	0.985
PVP-Br	0.645
1 : 1 Mixture (Calc)	0.860

present polyioncomplex.

For the purpose of examining the dissolved state of polyioncomplex in soluble region, the intrinsic viscosity  $[\eta]$  of PC was measured at 30°C in a solvent mixture having the composition:18:51:31 weight-% acetone-water-NaBr. Also the intrinsic viscosities of PSS-Na and PVP-Br were measured in the same solvent mixture. These experimental values were given in Table 1.

The intrinsic viscosity  $[\eta]$  of polymer mixtures, if specific interaction dose not exist between components, can be given by the equation

$$[\eta] = \sum w_i [\eta]_i$$

where  $[\eta]_i$  and  $w_i$  denote the intrinsic viscosity and weight fraction of the i-component, respectively. Representing the intrinsic viscosities of polycation and polyanion by  $[\eta]_{P^+}$  and  $[\eta]_{Q^-}$ , respectively, one obtains the following equation for 1:1 mole mixture of polycation and polyanion

$$[\eta] = 0.365 [\eta]_{P^+} + 0.635 [\eta]_{Q^-}$$

which leads to  $[\eta]=0.860$  for such 1:1 mole mixture. The experimentally obtained value of  $[\eta]=0.923$  for PC is about 7% higher than the value  $[\eta]=0.860$  calculated for model mixture. This difference in  $[\eta]$  may be attributed to that the polycation and polyanion do not behave perfectly independent but some electrostatic interaction may exist between polycation and polyanion, which leads to an increase in intrinsic viscosity. The role of NaBr (or  $\text{CaCl}_2$ ) may be to loosen the electrostatic interaction between polycation and polyanion, while acetone may interact to and stabilize the hydrophobic chain portions of these polyelectrolyte molecules. Further, water may act to hydrate on both polycation and polyanion, and behaves as diluent for acetone. Such transparent solution of polyioncomplex can produce filament and film by coagulating the solution.

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